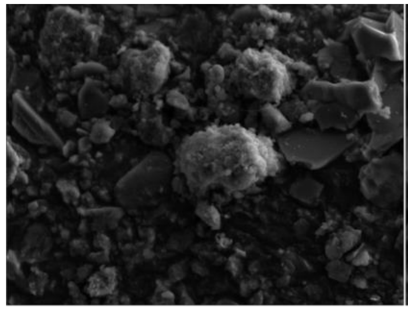
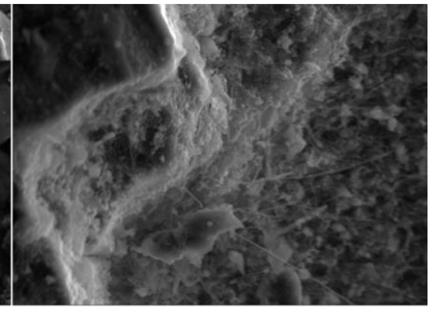
Center for Environmentally Sustainable Transportation in Cold Climates

Cost-Effective Use of Sustainable Cementitious Materials as Reactive Filter Media (Phase I)
Final Report



SEM micrograph of SiC525



SEM micrograph of RSiC525

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INE/CESTiCC 19.18

REPORT DOCUMENTATION PAGE			Form approved OMB No.
Public reporting for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-1833), Washington, DC 20503			
1. AGENCY USE ONLY (LEAVE BLANK)	2. REPORT DATE 08/2019	3. REPORT TYPE AND DATES COVERED Final Report: 11/2015 – 08/2019	
4. TITLE AND SUBTITLE Cost-Effective Use of Sustainable Cementitious Materials as Reactive Filter Media (Phase I Report)			5. FUNDING NUMBERS
6. AUTHOR(S) Wenbing Li, Ph.D., P.E., Washington State University, Wuhan University of Science and Technology Xianming Shi, Ph.D., P.E., Washington State University			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Laboratory of Advanced & Sustainable Cementitious Materials Washington State University 405 Spokane Street, Sloan 101, P.O. Box 755900 Pullman, WA, 99164			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Department of Transportation 1200 New Jersey Avenue, SE Washington, DC 20590			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLENMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT No restrictions			12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This report presents a laboratory study on the use of nano SiO_2 as modifier in crushed fines recycled concrete (CFRCs), coupled with thermal treatment, with the goal of fabricating a sustainable reactive medium to capture the chloride anions in deicer-laden stormwater runoff. A uniform design (UD) scheme was employed for the statistical design of experiments. Predictive models were developed based on the experimental data to quantify the influence of each design parameter on the effectiveness of removing Cl^- ions from simulated stormwater. The models were verified, and then employed for predictions. Finally, the samples of different CFRCs modified by nano SiO_2 and heating regimes were prepared under the optimal parameters identified via the Response Surface Methodology (*RSM*). The optimal processing of CRFCs include the use of admixing nano SiO_2 at 0.3% (by mass), then heating the material at 525ºC for 3h. The structure and properties of these CFRCs materials were characterized by XRD, FTIR, BET, SEM and EDS. These advanced characterization tools revealed that the modified CFRCs achieved great potential to chemically bind chloride anions. This work is expected to produce substantial benefits for highway agencies and other stakeholders of deicer stormwater runoff, through enhanced understanding of the efficacy and appropriateness of cementitious filter media in passive reactive systems for decreasing contaminant loading in stormwater runoff. The use of CRFCs as a low-cost sorbent will be economically attractive and environmentally sustainable, diverting them from waste stream and landfill and towards sustainable stormwater management.

14- KEYWORDS: Nano SiO_2, crushed fines recycled concrete, modify, chloride removal			15. NUMBER OF PAGES 111 16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT N/A

NSN 7540-01-280-5500

STANDARD FORM 298 (Rev. 2-98)
Prescribed by ANSI Std. 239-18 298-

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METRIC (SI*) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4		mm
ft	feet	0.3048		m
yd	yards	0.914		m
mi	Miles (statute)	1.61		km
		AREA		
in^2	square inches	645.2	millimeters squared	cm^2
ft^2	square feet	0.0929	meters squared	m^2
yd^2	square yards	0.836	meters squared	m^2
mi^2	square miles	2.59	kilometers squared	km^2
ac	acres	0.4046	hectares	ha
		MASS (weight)		
oz	Ounces (avdp)	28.35	grams	g
lb	Pounds (avdp)	0.454	kilograms	kg
T	Short tons (2000 lb)	0.907	megagrams	mg
		VOLUME		
fl oz	fluid ounces (US)	29.57	milliliters	mL
gal	Gallons (liq)	3.785	liters	liters
ft^3	cubic feet	0.0283	meters cubed	m^3
yd^3	cubic yards	0.765	meters cubed	m^3

Note: Volumes greater than 1000 L shall be shown in m^3

Symbol	When You Know	Multiply By	To Find	Symbol
		TEMPERATURE (exact)		
ºF	Fahrenheit temperature	5/9 (ºF-32)	Celsius temperature	ºC
		ILLUMINATION		
fc	Foot-candles	10.76	lux	lx
fl	foot-lamberts	3.426	candela/m^2	cd/cm^2
		FORCE and PRESSURE or STRESS		
lbf	pound-force	4.45	newtons	N
psi	pound-force per square inch	6.89	kilopascals	kPa

These factors conform to the requirement of FHWA Order 5190.1A *SI is the symbol for the International System of Measurements

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol When You Know Multiply By To Find Symbol

LENGTH

mm millimeters 0.039 inches in
m meters 3.28 feet ft
m meters 1.09 yards yd
km kilometers 0.621 Miles (statute) mi

AREA

mm^2 millimeters squared 0.0016 square inches in^2 m^2 meters squared 10.764 square feet ft^2 km^2 kilometers squared 0.39 square miles mi^2 ha hectares (10,000 m^2) 2.471 acres ac

MASS
(weight)

g grams 0.0353 Ounces (avdp) oz
kg kilograms 2.205 Pounds (avdp) lb mg megagrams (1000 kg) 1.103 short tons T

VOLUME

mL milliliters 0.034 fluid ounces (US) fl oz
liters liters 0.264 Gallons (liq) gal
m^3 meters cubed 35.315 cubic feet ft^3
m^3 meters cubed 1.308 cubic yards yd^3

TEMPERATURE
(exact)

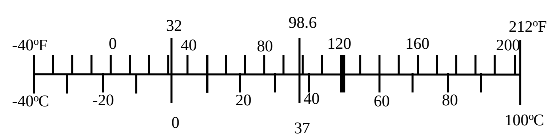
ºC Celsius temperature 9/5 ºC+32 Fahrenheit temperature ºF

ILLUMINATION

lx lux 0.0929 foot-candles fc
cd/cm^2 candela/m^2 0.2919 foot-lamberts fl

FORCE and PRESSURE or STRESS

N newtons 0.225 pound-force lbf
kPa kilopascals 0.145 pound-force per square inch psi



ACKNOWLEDGMENTS

The authors would like to thank the Center for Environmentally Sustainable Transportation in Cold Climates for funding this work. They would also like to thank Mr. Junliang Wu, Dr. Mehdi Honarvarnazari, Sen Du, and Jialuo He from the Laboratory of Advanced and Sustainable Cementitious Materials; faculty and staff from Dr. Scott Boroughs GeoAnalytical Lab and Dr. Qiang Zhang, Dr. Leiduan Hao Department of Chemistry at Washington State University, for their assistance in the laboratory investigations.

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EXECUTIVE SUMMARY

The primary objectives of this project were to: (1) evaluate the effectiveness of crushed fines from recycled concrete (CFRCs) with nano-modification (as reactive filter media) to treat synthetic surface runoff stormwater with high levels of chlorides and typical levels of total phosphorus, nitrogen and metals; and (2) unravel the mechanisms underlying contaminant removal by these engineered sorbents.

Nano SiO_2 was identified and tested as the modifier in crushed fines recycled concrete (CFRCs), coupled with thermal treatment. The statistical design of experiments employed a uniform design (UD) scheme. The project used predictive models developed based on the experimental data to quantify the influence of UD design parameters on the chloride removal in stormwater runoff. The models were verified and then employed for predictions.

Subsequently, the samples of different CFRCs modified by nano SiO2 and heating were prepared under the optimal parameters identified via the Response Surface Methodology (RSM). The optimal processing of CRFCs include the use of admixing nano SiO_2 at 0.3% (by mass), then heating the material at 525^{o}C for 3h. XRD, FTIR, BET, SEM and EDS characterized the structure and properties of these CFRCs materials. These advanced characterization tools revealed that the modified CFRCs achieved great potential to chemically bind chloride anions.

This work is expected to produce substantial benefits for highway agencies and other stakeholders of deicer stormwater runoff, through enhanced understanding of the efficacy and appropriateness of cementitious filter media in passive reactive systems for decreasing contaminant loading in stormwater runoff.

CHAPTER 1 INTRODUCTION

1.1 Background

The primary objectives of this project were to: (1) evaluate the effectiveness of crushed fines from recycled concrete (CFRCs) with nano-modification (as reactive filter media) to treat synthetic surface runoff stormwater with high levels of chlorides and typical levels of total phosphorus, nitrogen and metals; and (2) unravel the mechanisms underlying contaminant removal by these engineered sorbents.

Stormwater control is a national priority since non-point sources continue to rank as leading causes of water pollution. Many waters of the U.S. fail to meet the "fishable and swimmable" standard articulated by the U.S. Congress in 1977 with passage of Clean Water Act. As a major source of non-point source pollution, highway runoff has adverse effects on the adjacent aquatic resources if no measures are taken to remove the excessive contaminants accumulated from highway construction, maintenance and use. The EPA now requires the state DOTs to meet Total Maximum Daily Loads (TMDL) requirements and to restore the impaired waters. Cold climate may complicate the selection and performance of structural BMPs and present additional challenges. Frequent salting and sanding activities may increase sediment loads and produce large amounts of contaminants, and snowmelt and rain-on-snow events can produce large runoff volumes.

Recent years have seen increased use of coarse recycled-concrete aggregate (RCA) to partially replace virgin aggregate in concrete. Both RCA and CRFCs are produced by crushing concrete demolition waste, but CRFCs (the cementitious fine fraction) are significantly under-utilized. Wang et al. (2013) demonstrated the use of crushed concrete (7-10mm) and limestone to remove dissolved iron (Fe^{2+}) from synthetic groundwater, with effective removal capacities of 3.80 and 4.06 mg g^{-1}, respectively [1]. Coleman et al. (2005) reported the use of crushed concrete (1-2mm) to remove heavy metal species, Cu^{2+}(35 mg g^{-1}), Zn^{2+}(33 mg g^{-1}) and Pb^{2+}(37 mg g^{-1}) from aqueous media [2].

Cement-based materials (e.g., mortars and concretes) are commonly used to construct a significant portion of current wastewater systems, including septic tank and constructed wetland systems. However, our preliminary study (Wang et al. 2014) is the first one to demonstrate the use of ground powder of cementitious mortars to effectively remove phosphorus (P) from wastewater For three of them, the P-removal rates were in excess of 94% for P concentrations ranging from 20 to 1000mg/L[3]. The cement-based mortar exhibited the highest value of maximum adsorption (30.96 mg g^{-1}). The P-bonding energy (K_L) and adsorption capacity (K) exhibited a positive correlation with the total content of Al_2O_3 and Fe_2O_3 in each mortar. The maximum amount of P adsorbed (Q_m) and adsorption intensity ($1/n$) exhibited a positive correlation with the CaO content in each mortar.

There are a few studies [4-6] that demonstrated the effective use of nanomaterials to remove P or dyes from wastewater. However, the advantage has not been brought into play well because of the difficulties in dispersing or separating procedures [6].

Cement-based materials are known to be able to bind chlorides. In paste, mortar or concrete, chlorides can exist either in pore solution, chemically bound with the C3A (tricalcium aluminate) or C4AF phases (e.g., Friedel`s salt), or physically held to the surface of cement hydration products such as adsorption on C-S-H [7-9]. Carbonation of concrete can reduce the chloride-binding capacity (Neville 1995). Numerous factors affect the chloride-binding capacity, such as the C3A and alkali contents of cement [10], use of mineral admixtures [11], cation of the chloride salt [12], temperature, and degree of hydration [13].

1.2 Problem Statement

Chloride pollution due to the use of snow/ice control products on winter pavement is a significant source of water quality impairment. Chloride salts used as freezing point depressants (e.g., $NaCl$ and $MgCl_2$) are highly soluble in water and thus very difficult to remove from water bodies. They do not degrade in the environment and their accumulation thus poses a long-term risk for the quality of groundwater [14]. Transportation agencies need cost-effective tools to address this increasingly alarming issue. Nonetheless, current approaches in treating chloride-laden stormwater mainly rely on diversion and dilution, instead of removal of the chlorides.

In this context, we preliminarily assessed the use of crushed fines from recycled concrete (CFRCs) followed by some nano-modification for passive treatment of typical chloride-laden stormwater. Once saturated with contaminants, these filter media can be fully recycled in sustainable concrete applications. There is a lack of research investigating the use of CFRC or nano-modified reactive filter media for stormwater runoff treatment, let alone the performance evaluation of such engineered sorbents.

Research is needed to greatly advance our understanding in stormwater runoff treatment by low-cost engineered sorbents. For instance, our preliminary study [3] has revealed that both Langmuir and Freundlich adsorption isotherms are suitable for describing the P adsorption characteristics of cementitious materials. In this project, we elucidated the mechanistic role of nano-modified CFRCs in contaminant removal, with a focus on chlorides.

1.3 Scope of Work

This study placed the main emphasis on the preparation and evaluation of concrete-based materials by nano modifiers. The research plan included the following:

1. Planning: we reviewed the literature on the removal of chlorides from water through the method of adsorption and on the use of cement or concrete-based sorbents for ion removal.
2. Selection: we adopted the nano-modification procedure for obtaining the engineered sorbents that hold promise in effectively removing Cl- ions from synthetic stormwater.
3. Performance evaluation: we investigated the chloride removal performance of various nano-modified CFRCs as reactive filter media.
4. Mechanistic investigation: we employed X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM)/energy dispersive X-ray spectroscopy (EDS) to shed light on the chemical and physical characteristics of nano-modified CFRCs and thus unravel the mechanisms responsible for their better chloride removal efficiency.

1.4 Outline of Report

This report contains three chapters. Chapter 1 provides a description of the background and problem of interest and then outlines the scope of work. Chapter 2 describes the methodology and experimental results of the laboratory investigation on the nano-modified CFRCs for chloride removal from synthetic stormwater. Chapter 3 summarizes the work of this report and gives conclusions and recommendations for future research.

CHAPTER 2 MODIFIED THE CRUSHED FINES RECYCLED CONCRETE WITH NANO SiO2

2.1 Introduction

In cold climates, chlorides are the most commonly used freezing point depressant in roadway deicing and anti-icing products [15], typically including NaCl, $MgCl_2$ and $CaCl_2$. Chlorides can become a significant source of water quality impairment, in light of the large amount of deicing and anti-icing products used for snow and ice control on roadways and the fact that they do not degrade in the environment. High concentrations of chloride in wastewater can also cause problems in the biological treatment of the wastewater [16,17], and may induce corrosion of metallic pipes [18] or crop damage [19]. Chlorides are also capable of inducing corrosion of steel reinforcement in concrete [20]. Desalination of chloride-laden stormwater runoff is a necessary process for stormwater purification and may help mitigate the aforementioned risks.

Roadway agencies need to comply with increasingly stringent water quality regulations. This, along with a desire to minimize adverse environmental impacts, has led to the need for better management of stormwater challenges. Innovative and cost-effective solutions are much needed to address emerging water sustainability issues.

Several methods including ion exchange [21-23], membrane separation [24], liquid extraction [25], electroosmosis [26], and adsorption [27] technologies are adopted to remove the chloride in wastewater. The adsorption method attracts more attention due to the application of adsorbents with simplicity, effectiveness and low cost [28]. Crushed fines recycled concrete (CFRCs) from construction waste generated during the demolition of old infrastructure can hardly be reused in construction materials due to its weak mechanical stability [3, 29, 30]. Fortunately, CFRCs with the structure of cementation can be suitable as an adsorbent instead of high cost adsorbent of chloride [3,31]. Nanotechnology can be used to modify CFRCs for better adsorption [32]. Nano SiO_2 has been applied to modify concrete to improve the properties of concrete [33]. Then, CFRCS modified by nano SiO_2 may show better performance of chloride adsorption.

The rest of this Chapter describes an exploratory study that demonstrates the feasibility of using nano-modified CFRCs for the removal of chloride from stormwater runoff. This is a novel application of this construction waste (CFRCs), waste typically landfilled rather than utilized as a resource.

2.2 Experimental

2.2.1 Materials

The recycled concrete was obtained from a demolished concrete building on the Washington State University Pullman campus. After crushing and sieving, the fractions finer than #200 sieve (<75 µm) were used as the CFRCs in this study. Nano SiO_2 was purchased from Aldrich, CAS:7631-86-9, MW:60.08 g/mol, d:2.2-2.6 g/mL, at 25°C assay:99.5% trace metals basis. Sodium chloride was purchased from Aldrich, CAS: 7647-14-5.

2.2.2 Fabrication of modified CFRCs and testing methods

To further engineer the CFRCs, the samples were pretreated by drying at 100 degrees to constant weight and then placed in a crucible that was resistant to alkaline materials. Then the given proportion of inorganic modifier was added to the crucible. After mixing, the crucible was placed into the muffle furnace filled with nitrogen (without air). The temperature gradient (such as 500 °C,600 °C,700 °C,800 °C, etc) would be adjusted and calcined for a period of time, then the crucible was taken out of the furnace, and cooled to room temperature under the protection of nitrogen. Finally, the sample was placed into a desiccator without air.

To examine the CFRCs at the microlevel, scanning electron microscopy (SEM) occurred. The information about surface morphology and the amorphous and crystalline structure of the samples was obtained by using a JEOL JXA-8500F electron microprobe. The beam conditions used were as follows: 15 kV accelerating voltage, 50 nA beam current, and focused beam diameter. Specifically, secondary electron imaging (SEI) and backscattered electron imaging (BSE) were the two modes of the instrument used to obtain high-resolution images from microscopic areas of interest on each sample.

The researchers obtained FTIR spectra on a Thermo Scientific Nicolet™ iS™ 10 spectrometer with a Praying Mantis DRIFT accessory in the range of 4000−400 cm^{-1} with a resolution of 4 cm^{-1}. KBr was used as the background and a concrete powder sample was ground together with KBr powder before the measurement. N_2 adsorption data were collected on a Micrometrics ASAP 2020Plus accelerated surface area and porosimetry system at 77 K. Samples were activated under vacuum at 120 ºC for 12 h before gas adsorption experiments using the activation port of an ASAP 2020Plus instrument. Powder XRD patterns were collected for the samples at different modified conditions using an X-ray diffractometer with an incident beam of Cu-Kα radiation (λ= 1.5418 Å) for a scanning range of 0^o-80^o and mounted in a powder reservoir holder. XRD scans were compared with reference patterns in the International Centre for Diffraction Data (ICDD) Powder Diffraction File database (PDF) to identify mineral components.

2.2.3 Statistical design of experiment

Optimizing the significant parameters in the chloride removal process without statistical design is a time-consuming and complicated process for a multi-variable system [34]. Response surface methodology (*RSM*) is an effective technique for process optimization. In a minimal experiment, it can overcome the difficulty and gain an auxiliary equation that relates the independent variables with the response [35]. The use of a statistical design of experiment (DoE) enabled the exploration of a large domain of unknown factors and their interactions with a limited number of experiments.

In this study, the experimental results from the Uniform Design (UD) scheme were used to model and then optimize the process of chloride removal. A second order polynomial can be employed to obtain a significant model. For a response variable, a second order model is as follows [36]:

$$y=\beta_0 + \sum_{i=1}^{k} \beta_i \cdot X_i + \sum_{i=1}^{k} \beta_{ii} \cdot X_i^2 + \sum_{i<j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

Where y is the response variable, β_0, β_i, β_{ii}, and β_{ij} are offset term, linear coefficients, quadratic coefficients, interaction coefficients respectively. X_i and X_j are the independent variables.

Table 2. 1 Experimental range and levels of independent process variables

Variable	Factor	Range and level				
		-α	-1	0	1	+α
Temperature Celsius (ºC)	X1	473.22	525	650	775	826.78
Time (h)	X2	2.59	3	4	5	5.41
Content (%)	X3	0.18	0.3	0.6	0.9	1.02

Error! Reference source not found.1 presents the three design factors and their values at five different levels for UD. Fifteen experiments are conducted (Table 2.2). The Design Expert 7.0.0 software is used to assess the experimental data. The data are subjected to sequential sum of squares test and lack of fit test in order to select the most adequate model among the various models. ANOVA is employed to carry out data analysis as a function of each required response. Significant terms are usually identified at 95% confidence. The goodness of fit is determined from the values of R^2 obtained.

Table 2. 2 The UD scheme

Experiment number	Experimental design			Experiment plan		
	Temperature Celsius (°C)	Time (h)	Content (%)	X1	X2	X3
1	0	0	0	650.00	4.00	0.60
2	0	0	0	650.00	4.00	0.60
3	0	0	+α	650.00	4.00	1.02
4	1	-1	1	775.00	3.00	0.90
5	0	0	0	650.00	4.00	0.60
6	-α	0	0	473.22	4.00	0.60
7	-1	-1	-1	525.00	3.00	0.30
8	-1	1	1	525.00	5.00	0.90
9	0	-α	0	650.00	2.59	0.60
10	0	+α	0	650.00	5.41	0.60
11	0	0	0	650.00	4.00	0.60
12	1	1	-1	775.00	5.00	0.30
13	0	0	0	650.00	4.00	0.60
14	+α	0	0	826.78	4.00	0.60
15	0	0	-α	650.00	4.00	0.18

2.3 Results and Discussions

2.3.1 Optimizing the modified parameters by *RSM*

The experiments performed by RSM are based on mathematical techniques for investigating the relationship between variables of modified parameters. Three variables at five different levels were selected for optimization. These were: modify temperature, modify time, and the content of nano SiO_2 (Table 2.1). Table 2.2 depicts the experimental plans. In order to investigate the combined effect of three modified parameters (independent variables) on the chloride removal efficiency, 15 experiments were conducted for optimization of the modified parameters to remove chloride.

Table 2. 3 Central composite rotatable design (UD) matrix of independent variables and the corresponding experimental results (the response)

Experiment number	Variable			Removal efficiency (η,%)	
	Temperature Celsius (^{o}C)	Time (h)	Content (%)	Predicted	Experimental
1	0	0	0	42.74	41.22
2	0	0	0	42.74	41.22
3	0	0	+α	39.91	40.71
4	1	-1	1	63.36	62.56
5	0	0	0	42.74	41.22
6	-α	0	0	62.77	63.57
7	-1	-1	-1	65.41	**64.61**
8	-1	1	1	39.85	39.05
9	0	-α	0	61.29	62.09
10	0	+α	0	48.17	48.97
11	0	0	0	42.74	41.22
12	1	1	-1	60.84	60.04
13	0	0	0	42.74	41.22
14	+α	0	0	50.35	51.15
15	0	0	-α	52.45	53.25

Table 2.3 shows the predicted responses for chloride removal efficiency and the experimental results. The experimental values obtained from UD were regressed by a quadratic polynomial equation. Equation (1) represents the mathematical model relating the chloride removal efficiency with independent process variables, X_i, and the second-order polynomial coefficient for each term of the equation determined through multiple regression analysis using the software Design Expert. The experimental and predicted values of chloride removal efficiency are also given in Table 2.3.

Table 2. 4 ANOVA for Response Surface Quadratic Model

Source	Sum of squares	DF	Mean square	F value	Prob>F	Significant
Model	1297.47	9	144.16	201.28	0.0020	Yes
A-Temperature	77.13	1	77.13	10.80	0.0218	Yes
B-Time	86.07	1	86.07	12.05	0.0178	Yes
C-Content	78.63	1	78.63	11.01	0.0211	Yes
AB	3.52	1	3.52	0.49	0.5141	No
AC	11.34	1	11.34	1.59	0.2632	No
BC	166.57	1	166.57	23.32	0.0048	Yes
A^2	368.34	1	368.34	51.57	0.0008	Yes
B^2	277.25	1	277.25	38.82	0.0016	Yes
C^2	22.82	1	22.82	3.20	0.1339	No
Residual	35.71	5	7.14			
Lack of Fit	6.91	1	6.91	0.96	0.3827	
Pure Error	28.80	4	7.20			
Cor Total	1333.18	14				
Std. DEV	2.67		R-Squared		0.9732	
Mean	50.54		Adj-Squared		0.9250	
C.V.%	5.29		Pred R-Squared		0.4069	
PRESS	790.65		Adeq Precision		11.713	

The results were analyzed using ANOVA (Table 2.4). ANOVA of the quadratic regression model and model *F* value indicates the model to be significant. The model *F* value is calculated as ratio of mean square regression and mean residual. The model *P* value (Prob>*F*) is very low (0.0020), that shows the model is significant [35].

The regression model equation chloride removal efficiency in the coded form was obtained as follows:

Final Equation is presented as follows in terms of the Coded factors:

$$\text{Removal efficiency } (\eta)=42.74-4.39*A-4.64*B-4.43*C+1.33*A*B+2.38*A*C-9.13*B*C +6.91*A^2+ 5.99*B^2+ 1.72*C^2 \quad (2)$$

where A=Temperature Celsius, B=Time, C=Content are in coded units.

Final Equation in terms of Actual factors:

$$\text{Removal efficiency } (\eta)=361.98914-0.69059*A-41.24384*B+42.6926*C+0.010612*A*B$$
$$+0.063503*A*C-30.42044*B*C+4.42240E-4*A^2+5.99500*B^2+19.11111*C^2 \quad (3)$$

where A=Temperature Celsius (^{o}C), B=Time (h), C=Content (m/m, %) are in actual units.

The fit of the model was also expressed by the coefficient of determination, R^2, which was found to be 0.9732, indicating that 97.32% of the total variation in the response could be explained by the model. The value of the adjusted determination coefficient, adjusted R^2, which was found to be 0.9250, is also high to advocate for the significance of the model. These results could indicate that the predicted values exhibit a good correlation with experimental data and that the model is suitable and practicable.

The predicted versus actual plots for chloride removal efficiency is shown in Figure 2.1. The observed points on the plots reveal that the actual values are distributed relatively near to the straight line.

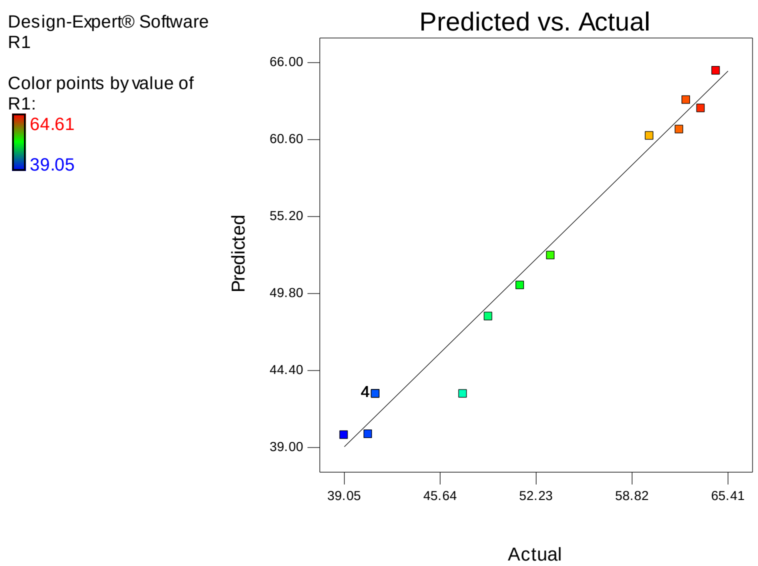

Figure 2. 1 Design-Expert plot. Predicted vs actual data for removal efficiency of chloride

Contour plots of the RSM are drawn as a function of two factors at a time, holding all other factors at fixed levels. Three-dimensional (3D) contour plots were provided to show response surface plots, which help to identify the type of interactions between test variables on the response in Figure 2.2-Figure2.4. Graphs given here highlight the roles played by significant factors.

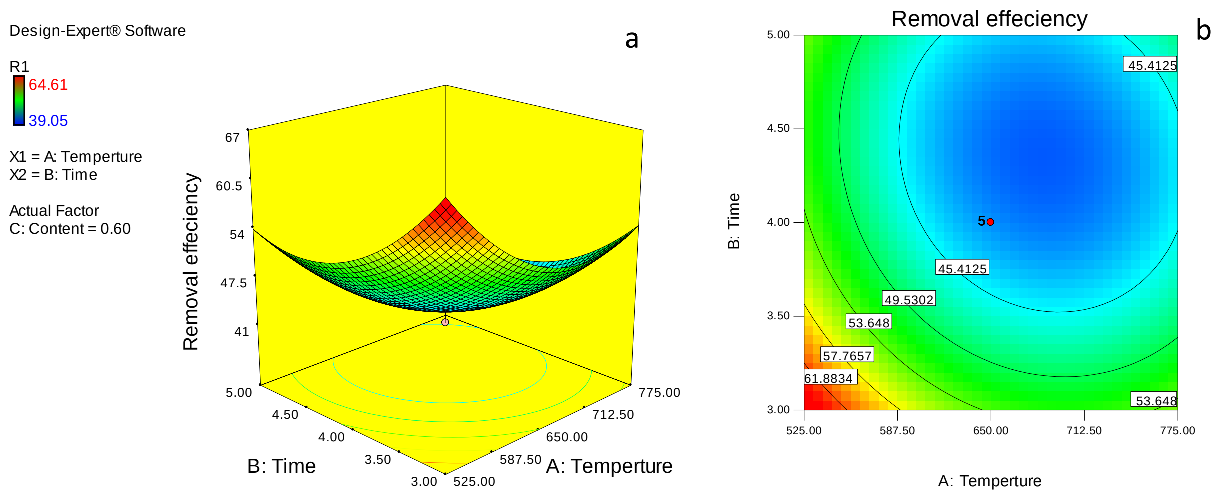

Figure 2. 2 Design-Expert plot. 3D surface graph (a) and contour graph (b) of removal efficiency of chloride showing the effect of temperature and time.

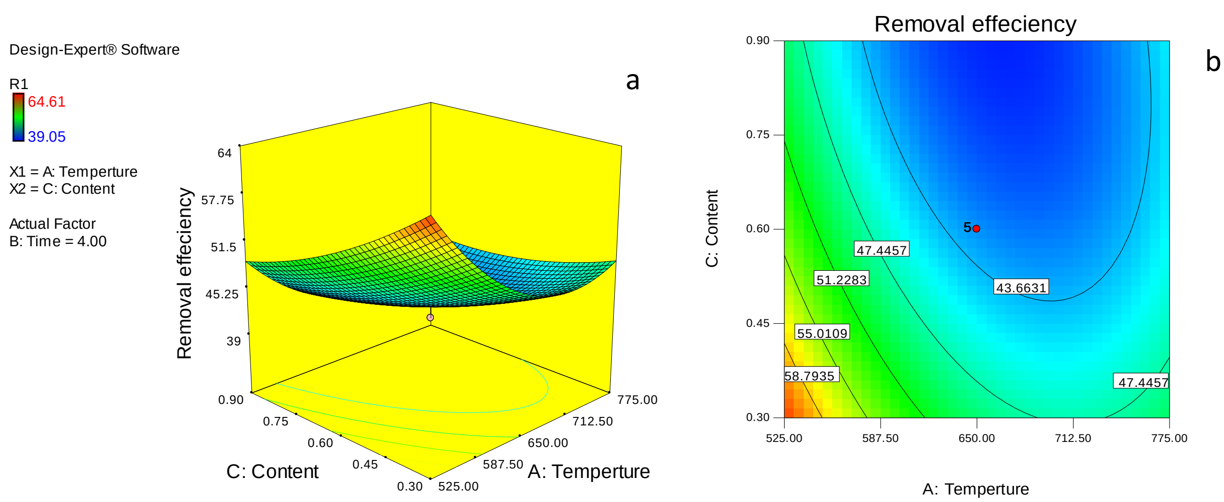

Figure 2. 3 Design-Expert plot. 3D surface graph (a) and contour graph (b) of removal efficiency of chloride showing the effect of temperature and content.

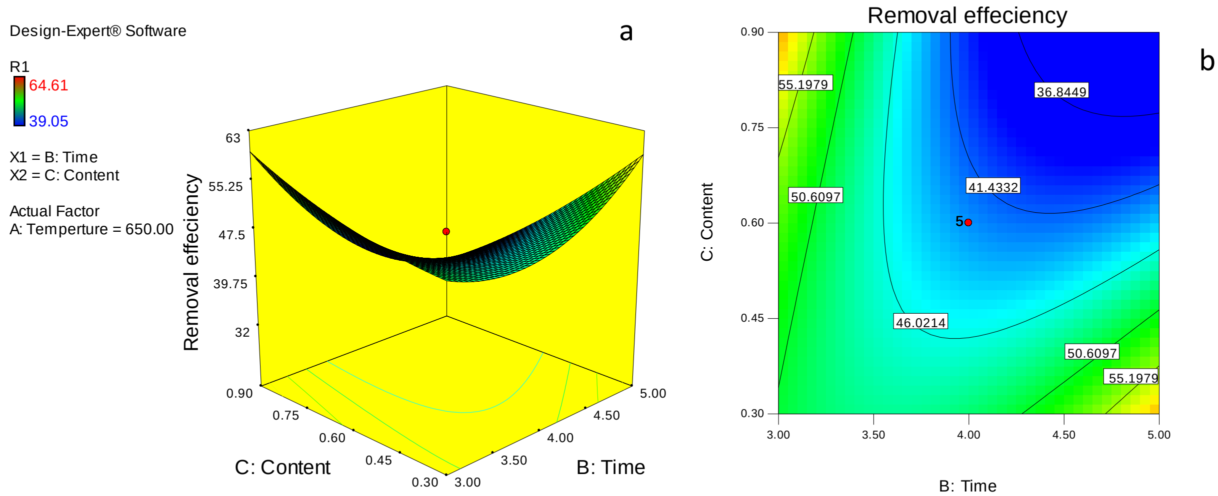

Figure 2. 4 Design-Expert plot. 3D surface graph (a) and contour graph (b) of removal efficiency of chloride showing the effect of time and content.

From the central point of the contour plot or from the bump of the 3D plot the optimal chloride removal efficiency was identified (Figure 2.2-Figure 2.4). The optimal modified parameters for the three factors from the maximum point of the model to be 525^{o}C of modified temperature, 3 hours of modified time, and 0.3% (m/m) of the content nano SiO_2, respectively. The predicted maximum removal efficiency of chloride was 65.41% under the optimum condition, which is in close agreement with the experimental value.

2.3.2 Model validation

In order to confirm the model accuracy and the results from the response surface response analysis, three experiments were performed randomly with the optimal parameters. The average removal efficiency of chloride obtained through the experiment was 65.76%. The experimental findings were in close agreement with the model prediction. Subsequently, samples were fabricated under the model-predicted optimal parameters and then subjected to advanced characterization tools such as XRD and SEM.

2.3.3 XRD analysis

Figure 2.5 and Figure 2.6 show the XRD patterns of the samples. The NC refers to the unmodified material of crushed fines recycled concrete (CFRCs), C525 refers to the CFRCs thermally modified at 525 ^{o}C, and SiC525 refers to the CFRCs thermally modified at 525 ^{o}C along with nano-SiO_2. RC525 and RSi525 refer to the samples of C525 and Si525 after being subjected to chloride exposure.

Figure 2.5 shows the XRD pattern of the NC, which was indexed to albite ($NaCaAl_4Si_3O_8$, PDF41-1480) or calcium aluminum silica hydrate ($Ca_4(Al_8Si_8O_{32}) \cdot (H_2O)_{17.21}$, PDF88-1189), and quartz (SiO_2,PDF85-1504). These crystalline phases have been reported for concrete, where the quartz diffractions are due to the sand. XRD pattern of the C525 shows that the phases in CFRCs could be transformed due to the thermal treatment [29,37]. Enstatite ($MgSiO_3$, PDF73-1937; $Mg_{0.916}Ca_{0.084}SiO_3$, PDF76-0524) and Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, PDF41-1451) appeared. XRD pattern of the RC525 shows that the composition and structure of RC525 changed during the process of chloride removal from stormwater, with the XRD peaks showing the patterns of anorthite ($Ca_{0.43}Na_{0.7}(Al_{0.92}Si_{1.08})O_4$, PDF09-0456) or muscovite ($(K_{0.93}Na_{0.07})$ $Al_{2.73}Fe_{0.16}Si_{3.1}O_{11.83}H_2$), PDF34-0175), Friedel's salt ($Ca_2Al(OH)_6Cl(H_2O)_2$, PDF78-1219), and Kuzel's salt ($Ca_4Al_2O_6Cl_2\cdot 10H_2O$, PDF19-0202).

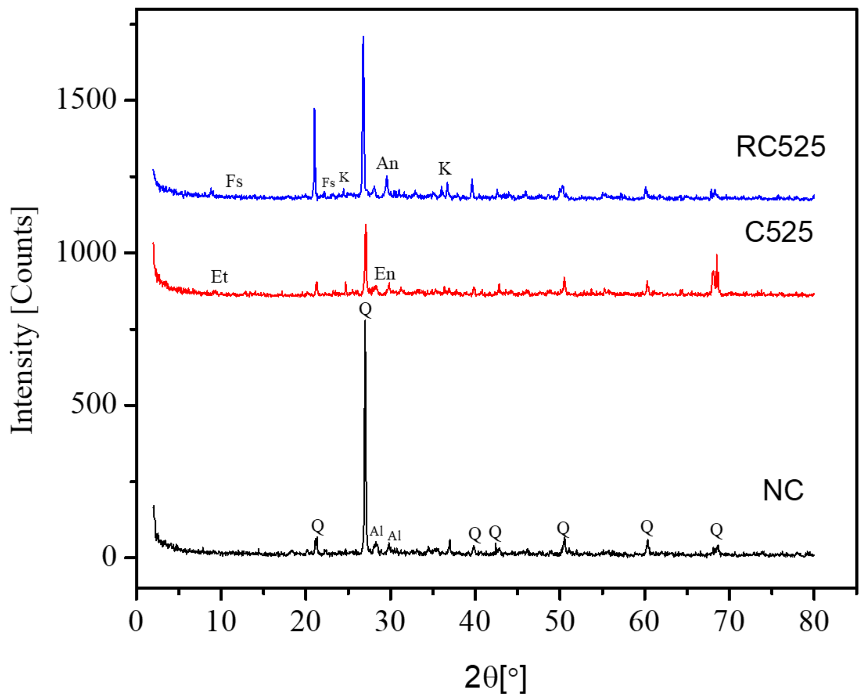

Figure 2. 5 XRD patterns of the samples of NC, C525 and RC525.Al: Albite, An: Anorthite, En: Enstatite, Et: Ettringite, Fs: Friedel's salt, K: Kuzel's salt, Q: Quartz.

Figure 2.6 shows the XRD patterns of SiC525 and RSiC525. The XRD of SiC525 shows that the XRD pattern of SiC525 compared with C525 forms Albite ($NaCaAl_4Si_3O_8$, PDF41-1480). The peaks of XRD pattern of RSiC525 was more significant than that RC525 reveals. Therefore, the structure and characteristics of the CFRCs were changed through the modified process of the thermal treatment and nano SiO_2 [38-40]. The chloride in stormwater can be effectively removed using the modified CRFCs.

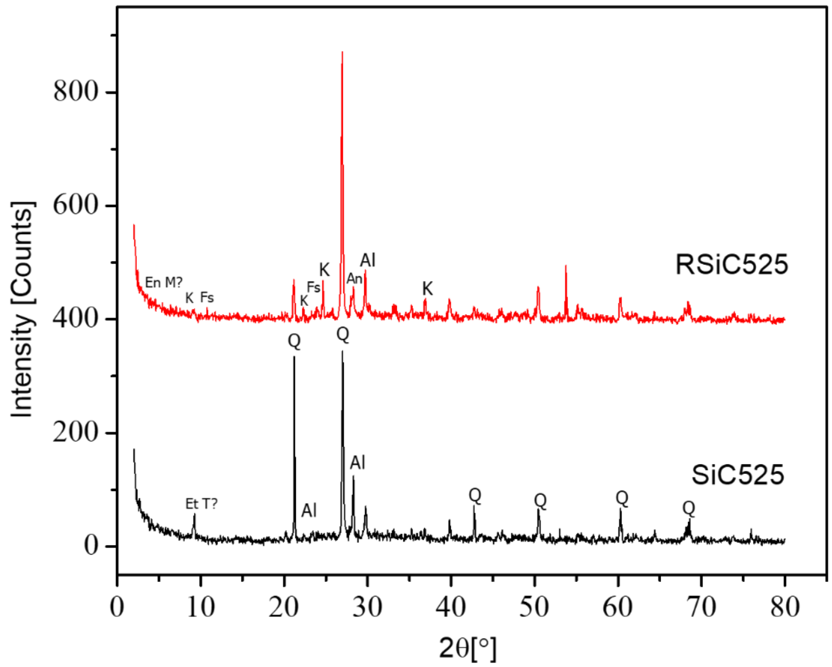

Figure 2. 6 XRD patterns of the samples of SiC525 and RSiC525.Al: Albite, An: Anorthite, En: Enstatite, Et: Ettringite, Fs: Friedel's salt, K: Kuzel's salt, M: Muscovite, Q: Quartz, T: Todorokite.

2.3.4 FTIR analysis

Table 2. 5 The samples of NC, C525, RC525, SiC525 and RSiC525 band assignments

band	NC (cm^{-1})	C525 (cm^{-1})	RC525 (cm^{-1})	SiC525 (cm^{-1})	RSiC525 (cm^{-1})	Assigned to
1	3634	3634	3634	3630	3630	vOH
2	1637	1647	1654	1637	1636	v_2H_2O
3	1484	1484	1484	1476	1484	vCO_3^{2-}
4	1146	1146	1146	1070	1059	vSi-O
5	978	978	978	990	976	vSi-O
6	877	877	877	873	875	$v_2CO_3^{2-}$
7	786	778	794	781	776	vAl-OH
8	686	686	686	691	687	vSi-O-Si
9	518	524	526	518	505	vAl-OH
10	452	452	452	465	447	vSi-O-Si

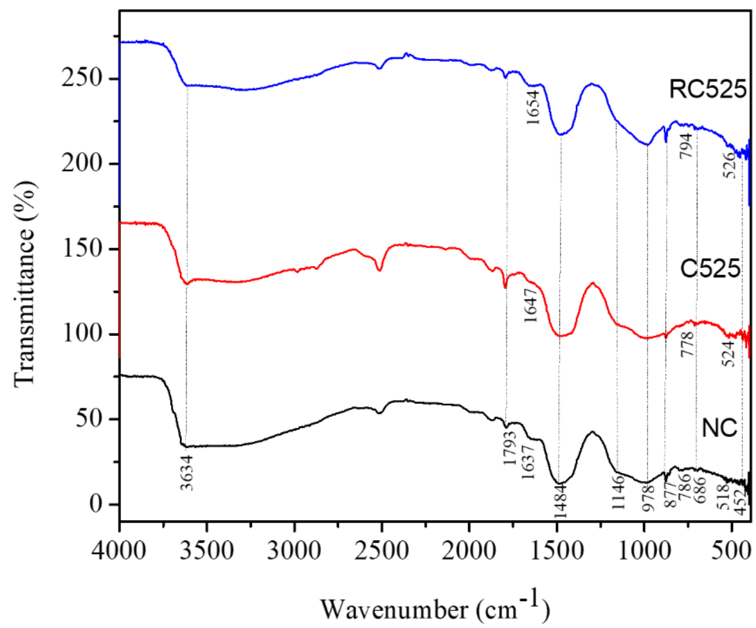

Figure 2. 7 FTIR spectra of the samples of NC, C525 and RC525.

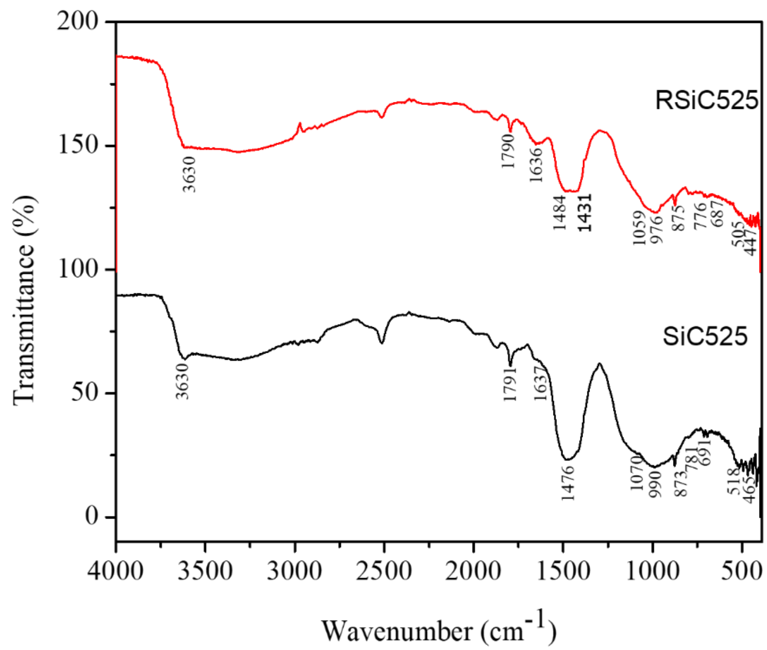

Figure 2. 8 FTIR spectra of the samples of SiC525 and RSiC525.

Figure 2.7 and Figure 2.8 present the infrared spectra of the samples. Table 2.5 gives the FTIR spectrum frequencies and band assignments. Band 4, 5 8, and 10 at 1059-1146, 976-990, 686-691, and 447-465 cm^{-1} show the characteristic of Si-O-Si deformation vibration. Band 3 and band 6 at 1476-1484 and 873-877 cm^{-1} show the characteristic of C-O stretching vibrations (CO_3^{2-}). Band 7 and band 9 at 505-526 and 776-794 $cm^{-1}$are ascribed to the bending and stretching vibration of Al-OH. Band 1 at 3630-3634 cm^{-1} is typical of OH stretching vibrations. The signals appearing at around 1636-1654 cm^{-1} is duo to the H-O-H bending vibration [41-43].

2.3.5 Adsorption isotherms

Adsorption isotherms of the samples of NC, C525, RC525, SiC525 and RSiC525 were determined by the BET and drift method, respectively. Figures 2.9 to Figure 2.11 are the adsorption-desorption isotherms of N_2 on NC, C525, RC525, SiC525, RSiC525. The figures suggest that these the adsorption-desorption isotherms belong to Brunauer type II. These results are presented in Table 2.6.

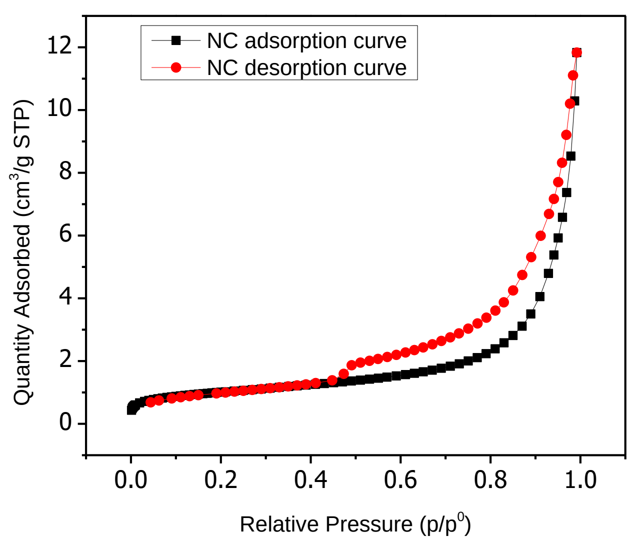

Figure 2. 9 Adsorption-Desorption BET curves for NC (unmodified CFRCs).

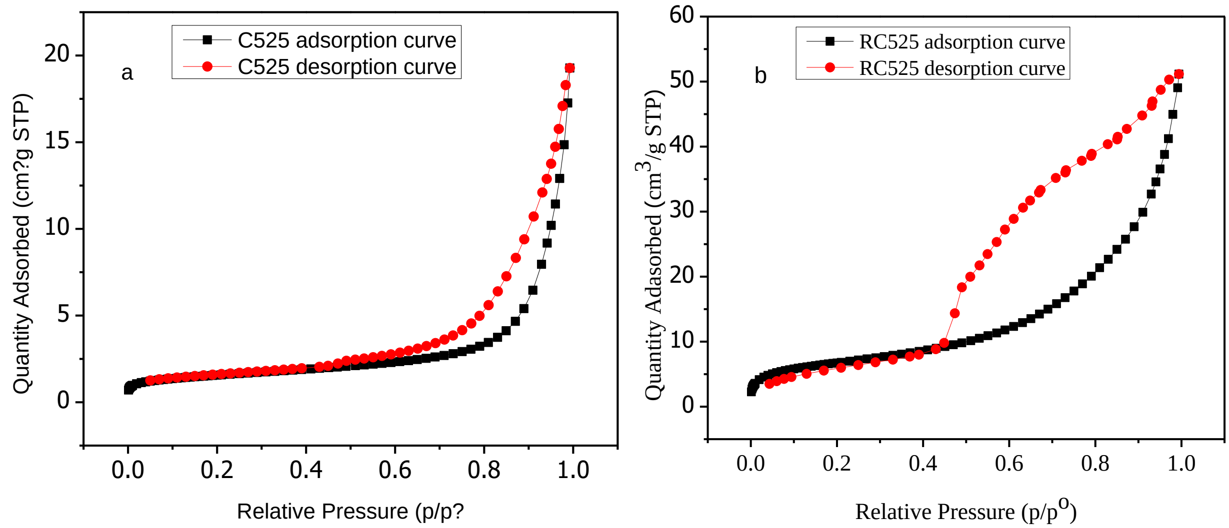

Figure 2. 10 Adsorption-Desorption BET curves for the samples: a, C525, modified CFRCs; b, RC525, chloride adsorption by modified CFRCs.

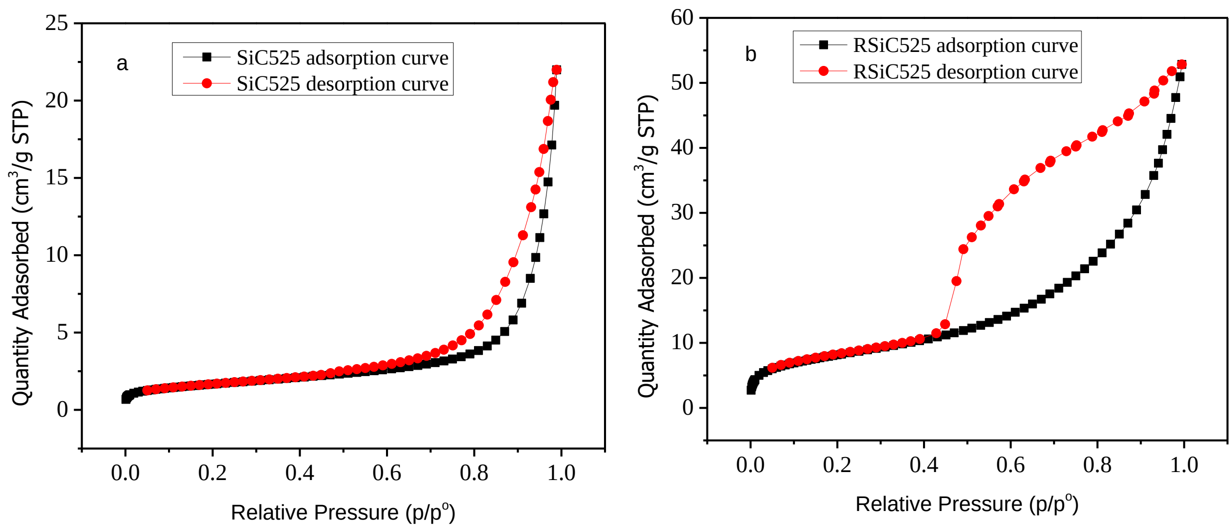

Figure 2. 11 Adsorption-Desorption BET curves for the samples: a, SiC525, modified CFRCs; b, RSiC525, chloride adsorption by modified CFRCs.

The BET surface areas of NC, C525, RC525, SiC525 and RSiC525 were 3.103, 4.9719, 20.5726, 5.0816 and 24.6596 m^2/g, respectively. The total pore volumes of NC, C525, RC525, SiC525 and RSiC525 were 0.01594, 0.02727, 0.06488, 0.02990 and 0.06021 cm^3/g respectively. The pore diameters in NC, C525 and SiC525 have slightly changed within the range of 2-7 nm, as shown in Table 2.6. The pore diameter of RC525 is close to that of RSiC525. The method of modification by thermal treatment along with added nano SiO_2 can improve the BET surface area by a substantial level [44,45], which translates to a higher availability of active surface sites for chloride adsorption.

Table 2. 6 Properties of the adsorbents

Material	S_{BET}, m^2/g	V_{total}, cm^3/g	V_{pore}, cm^3/g	D_{pore}, nm
RSiC525	24.6596	0.06021	0.061332	2-16
SiC525	5.0816	0.02990	0.017093	2-8
RC525	20.5726	0.06488	0.056475	2-14
C525	4.9719	0.02727	0.015656	2-7
NC	3.1503	0.01594	0.009114	2-7

2.3.6 SEM analysis

Figure 2.12a provides a representative SEM micrograph of the unmodified CFRCs (coded as NC, i.e., control). The crushed fines recycled concrete (CFRCs, NC) features non-uniform micrographs, that have layered, ellipsoidal shapes. The EDS spectrum of NC in Figure 2.12b shows the presence elements of C, O, Na, Mg, Al, Si, K, Ca, and Fe in NC, and suggest the presence of chemical constituents representative of ordinary silicate cement [46].

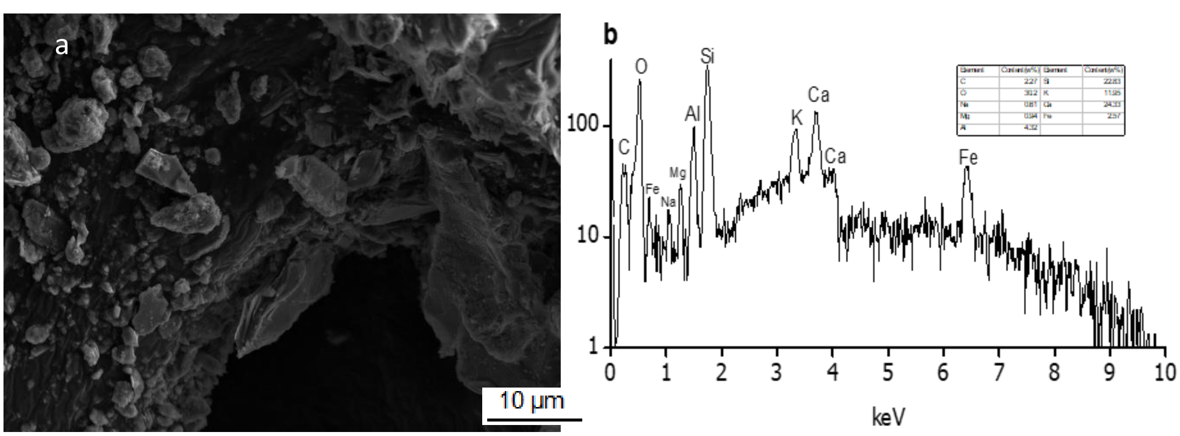

Figure 2. 12 SEM micrograph and EDS of unmodified CFRCs (NC). a: SEM, b, EDS.

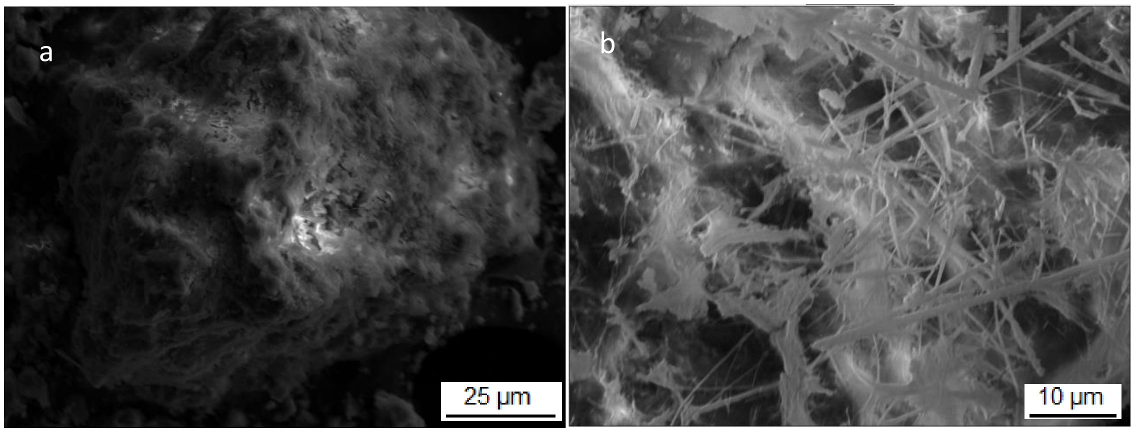

Figure 2. 13 SEM micrograph of the samples: a, C525, modified CFRCs; b, RC525, chloride adsorption by modified CFRCs.

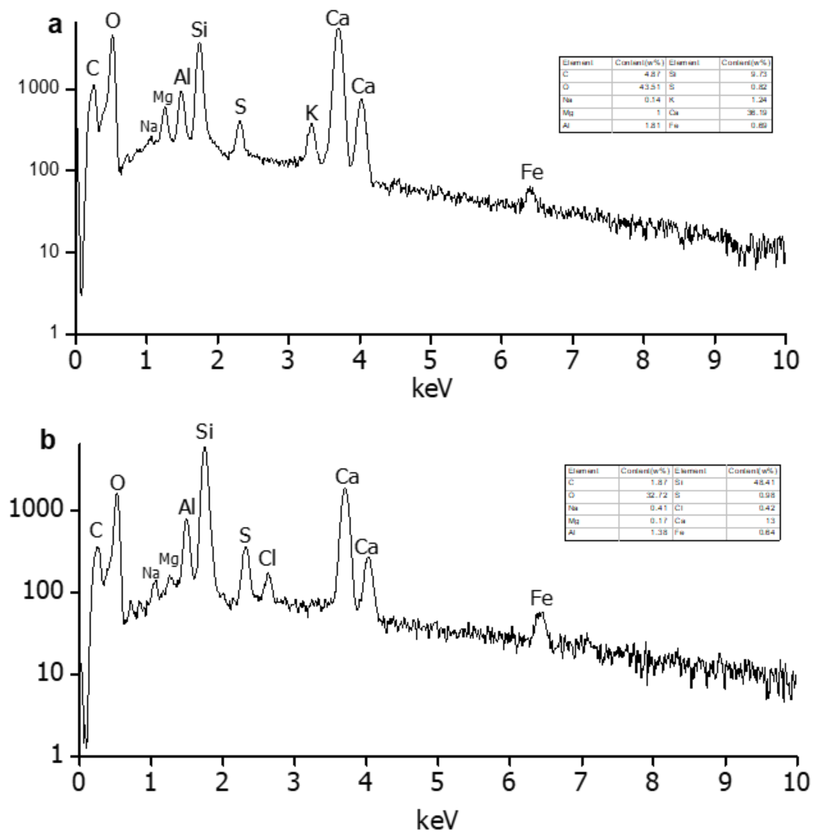

Figure 2. 14 EDS of the samples: a, C525, modified CFRCs; b, RC525, chloride adsorption by modified CFRCs.

The SEM micrograph of C525 in Figure 2.13a shows that the particles with ellipsoidal shape have more porosities and richer smooth surface than that in Figure 2.12a. This difference suggests that the structure of C525 could be transformed by thermal treatment. The SEM micrograph of RC525 in Figure 2.13b presents the new fibrous or filamentous structures, which suggests the occurrence of some reactions in the process of chloride removal from stormwater using C525 material. The EDS spectrum in Figure 2.14b indicates the transformations where chlorine appears.

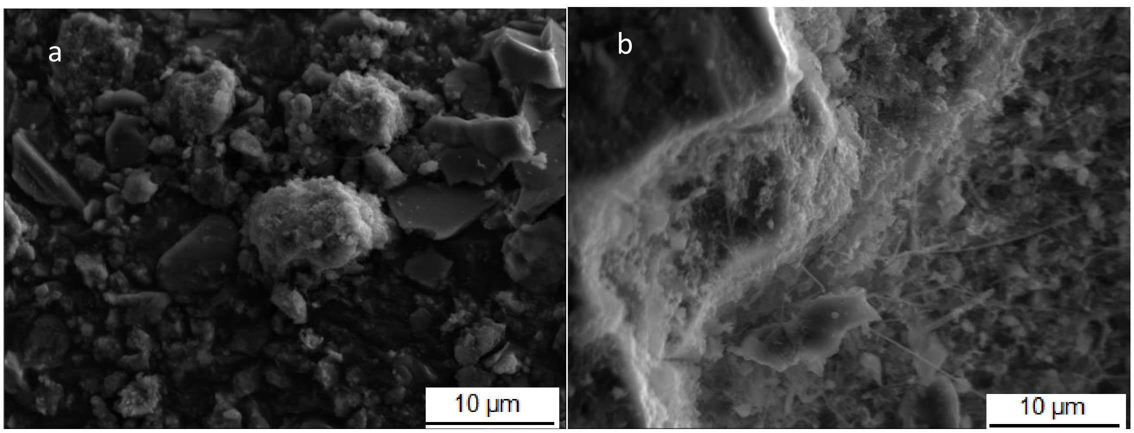

Figure 2. 15 SEM micrograph of the samples: a, SiC525, modified CFRCs with nano SiO_2; b, RSiC525, chloride adsorption by modified CFRCs with nano SiO_2.

The SEM micrograph of SiC525 in Figure 2.15a that the particles with ellipsoidal shape have more porosities, rich smooth surface and projects structures than that in Figure 2.13a, that means nano SiO_2 has great effect the structure of CFRCs with thermal treatment. The SEM micrograph of RSiC525 in Figure 2.15b presents the new stratified structures [47] and fibrous crystals that indicates there are significant changes in the process of chloride removal in stormwater using SiC525 material. The element analysis by EDS shown in Figure 2.16 indicates that the chlorine element adsorbed by SiC525 can form a new compound combined with other substances of SiC525. These new compounds form new crystalline structures shown in Figure 2.15b.

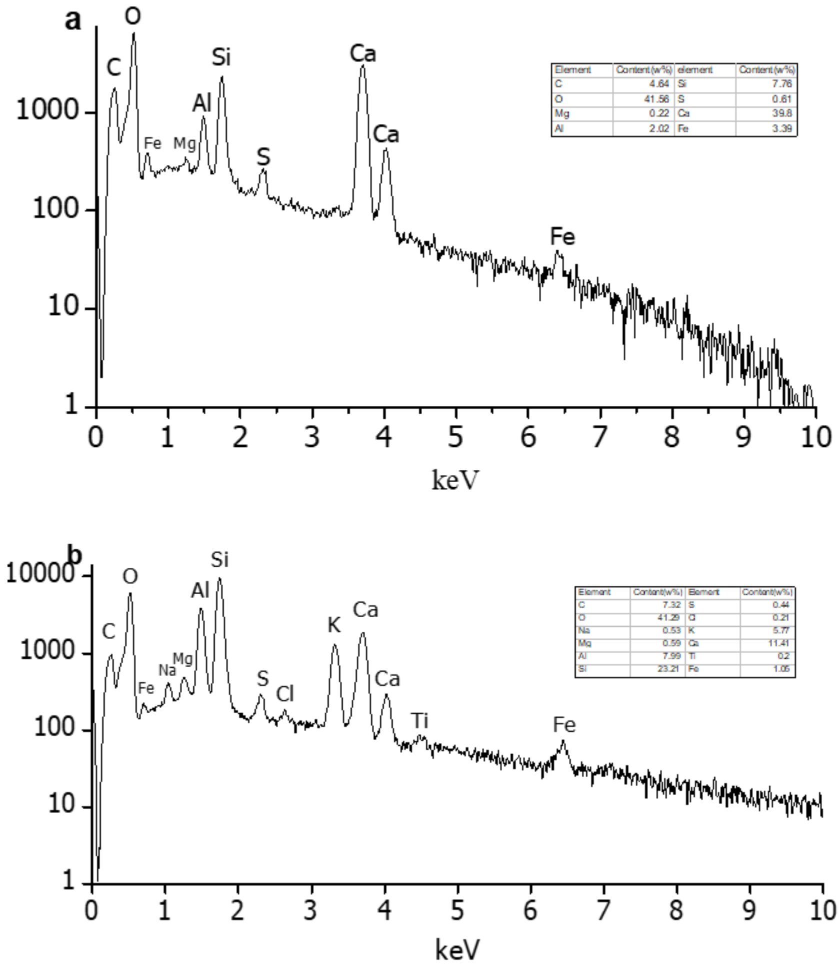

Figure 2. 16 EDS of the samples: a, SiC525, modified CFRCs with nano SiO_2; b, RSiC525, chloride adsorption by modified CFRCs with nano SiO_2.

2.4 Summary and Conclusions

The laboratory study in this chapter explores the beneficial use of nano SiO_2 as the modifier in crushed fines recycled concrete (CFRCs), coupled with thermal treatment. A UD scheme was employed for the statistical design of experiments. Predictive models were developed based on the experimental data to quantify the influence of design parameters on the chloride removal in stormwater. The models were verified and then employed for predictions. Subsequently, the samples of different CFRCs modified by nano SiO_2 and heating were prepared under the optimal parameters identified via the Response Surface Methodology (RSM). The optimal processing of CRFCs include the use of admixing nano SiO_2 at 0.3% (by mass), then heating the material at 525°C for 3h.

The XRD patterns of the samples of RC525 are similar to the patterns of anorthite ($Ca_{0.43}Na_{0.7}(Al_{0.92}Si_{1.08})O_4$) or muscovite ($(K_{0.93}Na_{0.07})Al_{2.73}Fe_{0.16}Si_{3.1}O_{11.83}H_2$), Friedel's salt ($Ca_2Al(OH)_6Cl(H_2O)_2$), and Kuzel's salt ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$). The XRD pattern of the RSiC525 indicates the presence of several phases, including Enstatite ($MgSiO_3$, $Mg_{0.916}Ca_{0.084}SiO_3$), Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), Albite ($NaCaAl_4Si_3O_8$), Friedel's salt and Kuzel's salt. The FTIR spectra also revealed the adsorption peak of these materials.

The BET adsorption isotherms by N_2 showed that the CFRCs modified by thermal treatment and addition of nano SiO_2 can improve the surface area of these sorbents by a substantial level. The increased surface area translates to a higher availability of active surface sites for chloride adsorption.

The SEM and EDS of RC525 and RSiC525 confirm changes due to the chlorine element adsorbed by C525 and SiC525, which formed new compounds and structures along with other substances of C525 and SiC525, respectively.

We conclude from the laboratory study that the CFRCs modified by nano SiO_2 and heating are capable of effectively removing chloride anions from stormwater.

CHAPTER 3 CONCLUSIONS

3.1 Summary

The primary objectives of this project were to: (1) evaluate the effectiveness of crushed fines from recycled concrete (CFRCs) with nano-modification (as reactive filter media) to treat synthetic surface runoff stormwater with high levels of chlorides and typical levels of total phosphorus, nitrogen and metals; and (2) unravel the mechanisms underlying contaminant removal by these engineered sorbents.

Nano SiO_2 was identified and tested as the modifier in crushed fines recycled concrete (CFRCs), coupled with thermal treatment. Researchers employed a uniform design (UD) scheme for the statistical design of experiments. Predictive models were developed based on the experimental data to quantify the influence of UD design parameters on the chloride removal in stormwater runoff. The models were verified and then employed for predictions.

Subsequently, the samples of different CFRCs modified by nano SiO2 and heating were prepared under the optimal parameters identified via the Response Surface Methodology (RSM). XRD, FTIR, BET, SEM and EDS characterized the structure and properties of these CFRCs materials. These advanced characterization tools revealed that the modified CFRCs achieved great potential to chemically bind chloride anions.

3.2 Key Findings

The optimal processing of CRFCs includes the use of admixing nano SiO_2 at 0.3% (by mass), then heating the material at 525ºC for 3 hours. Through use of the optimal parameters, the CFRCs modified by thermal treatment and addition of nano SiO_2 can improve the surface area of these sorbents by a substantial level. The increased surface area translates to a higher availability of active surface sites for chloride adsorption. After chloride removal from synthetic stormwater, new compounds and structures formed in the nano-modified CFRCs.

3.3 Expected Benefits

The project fits under the CESTiCC research thrust of "*managing stormwater runoff in cold climate through improved training, monitoring, advanced technology, and pervious concrete*".This work is expected to produce substantial benefits for highway agencies and other stakeholders of deicer stormwater runoff, through enhanced understanding of the efficacy and appropriateness of cementitious filter media in passive reactive systems for decreasing contaminant loading in stormwater runoff. The use of CRFCs as a low-cost sorbent will be economically attractive and environmentally sustainable, diverting them from the waste stream and landfills and towards sustainable stormwater management. The successful development of chloride sorbents based on CFRCs provides a template to incorporate other types of solid waste into engineered sorbents, thus reducing the need for consuming natural resources in such applications.

3.4 Recommendations for future research

- Stormwater treatment tests should be conducted to evaluate the long-term effectiveness of the filtration function provided by the nano-modified CFRCs. These tests can also investigate various stormwater runoff scenarios with varying initial chloride concentration and co-contaminant concentrations in the stormwater and possibly with more realistic simulation of wet-dry and temperature cycles.
- The structure of the nano-modified CFRCs should be further analyzed. For instance, XRD only sheds light on the crystalline phases, where other tools such as atomic pair distribution function (PDF) and thermal gravimetric analysis (TGA) may be employed

for quantification of amorphous phases in the engineered sorbents. In addition, the degree of polymerization and other chemical insights may be obtained by the use of Si and Al Nuclear Magnetic Resonance Spectroscopy (NMR).

- There is the need to investigate the best practice of recycling the contaminant-saturated filter media in concrete. The work will address the recyclability challenge related to contaminant-saturated filter media, thus minimizing the risk of secondary pollution. Traditionally, reactive media saturated with contaminants have been either landfilled or recycled as fertilizer or soil conditioner; in both cases, however, the leaching of metals out of them remains a great concern. We propose to recycle such materials in concrete, considering the following: concrete is a proven material for solidifying waste materials and both organic and metallic contaminants would be chemically bound in the concrete matrix, decreasing the rates of leaching to negligible levels. As such, experiments can be designed and conducted to assess the properties of concrete specimens incorporating saturated CFRCs as partial replacement of fine aggregate. The goal is to identify the appropriate replacement dosages at which the engineering properties of the concrete will not be significantly compromised. The metal leaching behavior of hardened concrete should also be tested in an accelerated manner.

REFERENCES

[1] Wang, Y., Sikora, S., & Townsend, T. G. Ferrous iron removal by limestone and crushed concrete in dynamic flow columns. *Journal of Environmental Management*, 2013, 124, 165-171.

[2] Coleman, N. J., Lee, W. E., & Slipper, I. J. Interactions of aqueous Cu^{2+}, Zn^{2+} and Pb^{2+} ions with crushed concrete fines. *Journal of Hazardous Materials*, 2005, 121(1), 203-213.

[3] Wang, X., Chen, J., Kong, Y., Shi, X. Sequestration of Phosphorus from Wastewater by Cement-Based or Alternative Cementitious Materials. *Water Research*,2014, 62(1), 88-96.

[4] Yuan, G., Wu, L. Allophane nanoclay for the removal of phosphorus in water and wastewater. *Science and Technology of Advanced Materials*, 2007, 8, 60-62.

[5] Liu, P., Zhang, L. Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents. *Separation and Purification Technology*, 2007, 58, 32-39.

[6] Yang, Q., Han, S., Fan, Q., & Ugbolue, S.C. Nanoclay and modified nanoclay as sorbents for anionic, cationic and nonionic dyes. *Textile Research Journal*, 2005, 75(8), 622-627.

[7] Berman HA. Determination of chloride in hardened Portland cement paste, mortar, and concrete. *J Mater,* 1972;7(3):330– 5.

[8] Harald J. A review of chloride binding in cementitious systems. *Nordic Concr Res,* 1998;21:1-6.

[9] Anik D, Jacques M, Jean-Pierre O, Simone J, Kati H. Chloride binding capacity of various hydrated cement systems. *Adv Cem Based Mater,* 1997;6:28– 35.

[10] Rasheeduzzafar, Hussain SE, Al-Saadoun SS. Effect of cement composition on chloride binding and corrosion of reinforcing steel in concrete. *Cem Concr Res*, 1991;21(5):777– 94.

[11] Shi, X., Xie, N., Fortune, K., & Gong, J. Durability of steel reinforced concrete in chloride environments: An overview. *Construction and Building Materials*, 2012, 30, 125-138.

[12] Andrade C, Page CL. Pore solution chemistry and corrosion in hydrated cement systems containing chloride salts: a study of cation specific effects. *Br Corros J*, 1986, 21(1):49-54.

[13] Buenfeld NR, Glass GK, Hassanein AM, Zhang J-Z. Chloride transport in concrete subjected to an electric field. *J Mater Civil Eng*, 1998,10(4):220– 8.

[14] Honarvar Nazari, M., Fay, L., Jungwirth, S., and Shi, X. (2015) Water Quality Implications and the Toxicological Effects of Chloride-Based Deicers. Environmental Sustainability in Transportation Infrastructure: pp. 272-292. ASCE Construction Institute. Special Publication. DOI: 10.1061/9780784479285.022.

[15] Fay, L., & Shi, X. (2010). Laboratory investigation of performance and impacts of snow and ice control chemicals for winter road service. *Journal of Cold Regions Engineering*, 25(3), 89-114.

[16] Panswad T., Anan C. Impact of high chloride wastewater on an anaerobic/anoxic/aerobic process with and without inoculation of chloride acclimated seeds. *Water Research*, 1999, 33(5):1165-1172.

[17] Lv L., He J., Wei M., Evans D.G., Duan X. Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies. *Water Research*, 2006, 40(4):737-743.

[18] Abdel-Wahab A., Batchelor B. Effects of pH, temperature, and water quality on chloride removal with ultra-high lime with aluminum process. *Water Environment Research*, 2006, 78(9):930-937.
[19] Hajrasuliha S. Accumulation and toxicity of chloride in bean plants. *Plant and Soil*, 1980,55(1): 133-138.
[20] Yoon S., Moon J., Bae S., Duan X., Giannelis E.P., Monteiro P.M. Chloride adsorption by calcined layered double hydroxides in hardened Portland cement paste. *Materials Chemistry and Physics*, 2014, 145(3):376-386.
[21] Popper K., Bouthilet R.J., Slamecka V. Ion-Exchange Removal of Sodium Chloride from Water with Calcium Hydroxide as Recoverable Regenerant. *Science*, 1963, 141(3585):1038-1039.
[22] Carmona M., Perez A., de Lucas A., Rodriguez L., Rodriguez J.F. Removal of chloride ions from an industrial polyethylenimine flocculant shifting it into an adhesive promoter using the anion exchange resin Amberlite IRA-420. *Reactive and Functional Polymers*, 2008, 68(8):1218-1224.
[23] Abu-Arabi M.K., Emeish S., Hudaib B.I. Chloride removal from Eshidiya phosphate mining wastewater. *Desalination and Water Treatment*, 2013, 51:1634-1640.
[24] Grygolowicz-Pawlak E., Sohail M., Pawlak M., Neel B., Shvarev A., Marco R. De, Bakker E. Coulometric Sodium Chloride Removal System with Nafion Membrane for Seawater Sample Treatment. *Analytical Chemistry*, 2012, 86: 6158-6165.
[25] Li Y., Song X., Chen G., Sun S., Xu Y., Yu J. Extraction of hydrogen chloride by a coupled reaction-solvent extraction process. *Front Chem Sci Eng*, 2015, 9(4):479-487.
[26] Andrade C., Castellote M., Sarria J., Alonso C. Evolution of pore solution chemistry, electro-osmosis and rebar corrosion rate induced by realkalisation. *Materials and Structures*, 1999, 32(6):427-436.
[27] Acelas N.Y., Florez E. Chloride adsorption on Fe- and Al-(hydr)oxide: estimation of Gibbs free energies. Adsorption, 2018, 24(3):243-248.
[28] Chen Q., Lan Q., Li, X., Zhou J., Yang Z., Zhou Y. Utilization of fine powder in demolition concrete as recyclable coagulant in removing color from dye-bearing waswater. *Environ Earth Sci*, 2015, 74: 6737-6745.
[29] Kang K., Lee C.-G., Choi J.-W., Hong S.-G., Park S.-J. Application of thermally treated crushed concrete granules for the removal of phosphate: A cheap adsorption with high adsorption capacity. *Water Air Soil Pollut*, 2017, 228:8.
[30] Zha Z., Ren Y., Wang S., Qian Z., Yang L., Cheng P., Han Y., Wang M. Phosphate adsorption onto thermally dehydrated aluminate cement granules. *RSC Adv*, 2018, 8: 19326-19334.
[31] Kagne S., Dhawade P.D., Kamble S.P., Rayalu S.S. Hydrate cement: A promising adsorbent for the removal fluoride from aqueous solution. *Journal of Hazardous Materials*, 2008, 154: 88-95.
[32] Said A.M., Zeidan M.S., Bassuoni M.Y., Tian Y. Properties of concrete in corporation nano-silica. *Construction and Building Materials*, 2012, 36:838-844.
[33] Zhou Y., Hou D., Jiang J., Wang P. Chloride ions transport and adsorption in the nano-pores of silicatecalcium hydrate: Experimental and molecular dynamics studies. *Construction and Building Materials*, 2016, 126:991-1001.
[34] Khan S.,U., Islam D.T., Farooqi I.ZH., Ayub S., Basheer F. Hexavalent chromium removal in an electrocoagulation column reactor: Process optimization using UD, adsorption kinetics

and pH modulated sludge formation. *Process Safety and Environmental Protection*, 2019,22:118-130.
[35] Zhang L., Yue Y. Influence of waste glass powder usage on the properties of alkali-activated slag mortars based on response surface methodology. *Construction and Building Materials*, 2018, 181:527-534.
[36] Li W., Cai L., Wu Y., Liu Q., Yu H., Zhang C. Assessing recycled pavement concrete mechanical properties under joint action of freezing and fatigue via RSM. *Construction and Building Materials*, 2018, 164: 1-11.
[37] Mesbah A., Rapin J.P., Francois M., Cau-dit-Coumes C., Frrizon F., Leroux F., Renaudin G. Crystal structures and phase transition of cementitious bi-anionic AFm-(Cl^-, CO_3^{2-}) compounds. *J Am Ceram Soc*, 2011, 94(1): 261-268.
[38] Grishchennko R.O., Emelina A.L., Makarov P.Y. Thermodynamic properties and thermal behavior of Friedel`s salt. *Thermochimica Acta*, 2013, 570: 74-79.
[39] Mesbah A., Francois M., Cau-dit-Coumes C., Frizon F., Filinchuk Y., Leroux F., Ravaux J., Renaudin G. Crystal structure of Kuzel`s salt $3CaO \cdot Al_2O_3 \cdot 1/2CaSO_4 \cdot 1/2CaCl_2 \cdot 11H_2O$ determined by synchrotron powder diffraction. *Cement and Concrete Research*, 2011, 41: 504-509.
[40] Paul G., Boccaleri E., Buzzi L., Canonico F., Gastaldi D. Friedel`s salt fromation in sulfoaluminate cements: A combined XRD and ^{27}Al MAS NMR study. *Cement and Concrete Research*, 2015, 67: 93-102.
[41] Yoysuf M., Molah A., Hess T.R., Tsai Y.N., Cocke D.L. An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-Portland type V with zinc. *Cement and Concrete Research*, 1993, 23: 773-784.
[42] Garcia Lodeiro I., Macphee D.E., Palomo A., Fernandez-Jimenez A. Effectof alkalis on fresh C-S-H gels. FTIR analysis. *Cement and Concrete Research*, 2009, 39: 147-153.
[43] Birnin-Yauri U.A., Glasser F.P. Friedel`s salt, $Ca_2Al(OH)_6(Cl,OH) \cdot 2H_2O$: its solid solutions and their role in chloride binding. *Cement and Concrete Research*, 1998, 28: 1713-1723.
[44] Odler I. The BET-specific surface area of hydrated Portland cement and related materials. *Cement and Concrete Research*, 2003, 33: 2049-2056.
[45] Wang L., Chen L., Wang H, Liao D. The adsorption refrigeration characteristics of alkaline-earth metal chlorides and its composite adsorbents. *Renewable Energy*, 2009, 34: 1016-1023.
[46] Qudoos A., Rehmam A., Kim H.G., Ryou J.S. Influence of the surface roughness of crushed natural aggregates on the microhardness of the interfacial transition zone of concrete with mineral admixtures and polymer latex. *Construction and Building Materials*, 2018,168:946-957.
[47] Ma J., Li Z., Zhang Y., Demopoulos G.D. Desilication of sodium aluminate solution by Friedel's salt (FS: $3CaO \cdot A1_2O_3 \cdot CaCl_2 \cdot 10H_2O$). *Hydrometallurgy*, 2009, 99: 225-230.